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(54) SUPERCONDUCTIVE WIRE AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a superconductive wire with high Jc and provide a manufacturing method of the superconductive wire.

SOLUTION: The manufacturing method includes a process to form a joined body by joining an oxide superconductive body or its precursor to a metal phase having 95% or higher orientation degree of a specified crystal plane and a process to adjust the c-axis orientation degree of the oxide superconductor body joined to the metal phase to be 95% or higher and the a- and b-axes conformity degree to be 75% or higher and by the method, the metal phase is made to be a polycrystalline body having 95% or higher orientation degree of a specified crystal plane and the crystal grains of the metal phase is made to have 2mm or longer length in the longitudinal direction, 4 or higher aspect ratio of the longitudinal direction to the width direction and the oxide superconductive body is made to have 95% or higher c-axis orientation degree and 75% or higher a- and b-axes conformation degree.

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CLAIMS

[Claim(s)]
[Claim 1] It is the superconduction line by which said metal phase is the polycrystalline substance whose amount of preferred orientation of the specific crystal face is 95% or more, the aspect ratio of 2mm or more, a longitudinal direction, and the cross direction of the crystal grain of this metal phase is [the die length of a longitudinal direction] four or more, and said oxides superconductors are characterized by for whenever [c-axis oriented] being 95% or more, and a and b-axis coherency being 75% or more in the superconduction line which a metal phase comes to join to oxides superconductors.
[Claim 2] The manufacture approach of the superconduction line according to claim 1 characterized by heating the process which joins oxides superconductors or its precursor to the metal phase whose amount of preferred orientation of the specific crystal face is 95% or more, and forms a zygote, and this zygote, and having the process which makes a and b-axis coherency 75% or more for whenever [c-axis oriented / of the oxides superconductors joined to the metal phase] 95% or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to an oxide superconductivity line and its manufacture approach.
[0002]
[Description of the Prior Art] As for the conventional oxide superconductivity line, the thing of the following structures is known.
1) It is the wire rod which carried out junction covering of the Bi system oxides superconductors with the silver of the polycrystalline substance, or the sheath of a silver alloy (reference 1, 2 reference). The crystal conformation of a and a b-axis has [this wire rod] the crystal stacking tendency of the c-axis of oxides superconductors as bad as 60% or less about 90%. consequently, critical current density Jc in 77K of a Bi system 2223 phase wire rod, and a zero tesla at most -- 4 - 6x104 A/cm2 It is extent. Jc [in / incidentally / Bi system single crystal thin film] 3x106 A/cm2 It is extent. However, this wire rod has a manufacture rate as quick as 100 m/h, and is industrially attractive.
Reference 1:ISTEC Journal Vol.8 and No. -- 2, 1995, pp.48-50 reference 2:ISTEC Journal Vol.8, and No. -- 2, 1995, and pp. -- 50-53 [0003] 2) Form Y system oxide superconductivity object with the laser ablation method, a CVD method, etc. on the substrate which carried out crystal orientation control by the ion beam assisting method etc. (reference 3 reference). this wire rod -- for example, the Hastelloy tape top -- the ion beam assisting method -- fully stabilized zirconia YSZ -- a -- b-axis adjustment (in-plane orientation) membrane formation is carried out, and it considers as the tape wire rod of a Y system 123 phase oxide superconductivity thin film by the laser ablation method. Since a and the crystal coherency of a b-axis are high, this tape is Jc. 0.5 - 1.1x106 A/cm2 It reaches. However, the fault of this process has a membrane formation rate very as slow as 0.001 - 0.01 m/h, and in order to manufacture a long wire rod, it is industrially unsuitable.
Reference 3:ISTEC Journal Vol.8 and No. -- 2, 1995, and pp. -- 43-45 [0004] 3) Form Y system and Tl system oxides superconductors by PVD, CVD, and the spray pyrolysis method to the polycrystal silver substrate which carried out organization control with recrystallization (reference 4 reference). This wire rod performs texture (001) control (about 50% of amounts of preferred orientation) for the silver which serves as a substrate beforehand by machining and recrystallization heat treatment, for example, and forms Tl system 1223 phase oxides superconductors by the spray pyrolysis method on this. Since critical temperature is high (122K), it is [that the silver substrate is making orientation about (001) 50% in this process, and] Jc. It is comparatively high and is 9x104 A/cm2. It reaches. However, orientation-ization of the silver by the recrystallization heat-treating method is a limitation mostly, and is Jc beyond this. The improvement in a property is ******.
Reference 4:ISTEC Journal Vol.8 and No. -- 2, 1995, and pp. -- 46-48 [0005] 4) Form Y system oxides superconductors on a nonmetal single crystal substrate by the liquid-phase-epitaxial method (reference 5 reference). This wire rod is annealed in about 450-degree C oxygen air current after forming Y system 123 phase from the 980-1000-degree C liquid phase for example, on a MgO (100) single crystal

substrate. The wire rod by this process is Jc although it has not realized yet. If 1x105 A/cm2 is reached and it can run a single crystal substrate, wire-rod-izing is possible. Moreover, this process is made possible [making a membrane formation rate into 0.01 - 1 m/h]. However, in this process, there is a fault for which mixing or membrane formation temperature of an unusual appearance by that it is necessary to rotate a substrate with 180rpm extent, a limit of melt-proof crucible material, and self flux use cannot use a silver substrate more highly than the silver melting point.
Reference 4:ISTEC Journal Vol.8 and No. -- 2, 1995, and pp. -- 19-23 [0006]
[Problem(s) to be Solved by the Invention] As mentioned above, the conventional oxide superconductivity line is Jc. There was a problem that industrial productivity was bad (structure of the 2nd and 4), low (structure of the 1st and 3).
[0007]
[Means for Solving the Problem] This invention is what was made that the above-mentioned trouble should be solved. Invention according to claim 1 In the superconduction line which a metal phase comes to join to oxides superconductors said metal phase The amount of preferred orientation of the specific crystal face is the polycrystalline substance which is 95% or more. The crystal grain of this metal phase The die length of a longitudinal direction is [the aspect ratio of 2mm or more, a longitudinal direction and the cross direction] four or more, whenever [c-axis oriented] is 95% or more, and said oxides superconductors are characterized by a and b-axis coherency being 75% or more.
[0008] Here, the specific crystal face and the amount of preferred orientation F of a c-axis are the specific crystal face of the polycrystalline substance which is carrying out completely random orientation, and the X diffraction reinforcement of a c-axis P0 It is expressed with F(%) =(P-P0)/(1-P0) x100, when it carries out and the actual specific crystal face and X diffraction reinforcement of a c-axis are set to P. However, X diffraction reinforcement P in the case of carrying out orientation in the fixed direction 100% is set to 1. When completely random orientation is being carried out from the upper type (P=P0), it is F= 0%, and when orientation is being completely carried out in the fixed direction (P= 1), it is F= 100%. Moreover, a and b-axis coherency show how much the a-axis or b-axis of crystal grain which is carrying out c-axis oriented is carrying out orientation in the fixed direction, completely, the case of being random is made into 0%, the case where it has consistency completely is made into 100%, and it asks like the case of the amount of preferred orientation F of an above-mentioned c-axis.
[0009] Moreover, invention according to claim 2 is the manufacture approach of the superconduction line according to claim 1 characterized by heating the process which joins oxides superconductors or its precursor to the metal phase whose amount of preferred orientation of the specific crystal face is 95% or more, and forms a zygote, and this zygote, and having the process which makes a and b-axis coherency 75% or more for whenever [c-axis oriented / of the oxides superconductors joined to the metal phase] 95% or more.
[0010] Invention according to claim 1 can realize high Jc (105 - 106 A/cm2) by such superconduction line of the crystal structure based on the result in which it experimented wholeheartedly. By such superconduction line of the crystal structure, since the metal phase which touches oxides superconductors is carrying out crystal orientation to altitude, this becomes a substrate and hetero epitaxial-growth of oxides superconductors is promoted. Consequently, Jc by which a and b-axis coherency also become very high, and are greatly governed by a and b-axis coherency not to mention whenever [c-axis oriented / of oxides superconductors] That to which a value becomes high as compared with the former can be considered.
[0011] Moreover, in invention according to claim 2, even if the metal phase which touches oxides superconductors passes through processes, such as a boring generally used in the manufacture process of a wire rod to 95% or more since crystal orientation control is carried out, extrusion, a wire drawing, and rolling, beforehand, if this metal phase finally has a suitable annealing process, it will hardly spoil a crystal stacking tendency. Therefore, in the phase where oxides superconductors are finally formed, the amount of preferred orientation of a metal phase is maintained, and can expect improvement in the crystal orientation of oxides superconductors.
[0012]

[Embodiment of the Invention] As a means which forms a metal phase into high orientation (95%), a unidirectional solidification method is applicable. By this approach, since desired magnitude and the metal (for example, major-diameter rod, tubing, line, tape, etc.) phase of a configuration are obtained, manufacture of a long wire rod is suited. Incidentally, by the processing recrystallizing method, even if the crystal amount of preferred orientation optimizes processing conditions 50% by tape material, it is made at most into 75%.

[0013] Moreover, which amorphous precursor can be used in the process in which the oxides superconductors which touch a metal phase are obtained. For example, since the amorphous precursor of oxides superconductors can be made to be able to solidify in contact with the metal phase orientation-ized by altitude and oxides superconductors can be formed with solid heteroepitaxial growth in a heating process, in spite of being a solid phase process, high Jc (105 - 106 A/cm2) can be obtained.

[0014]

[Example] Hereafter, the example of this invention is explained to a detail.

(Example 1) What was blended so that it might be set to :(Bi+Pb) Sr:calcium:Cu=2:2:2:3 by the mole ratio as oxides-superconductors raw material powder was prepared, CIP (hydrostatic pressing) shaping was carried out, and two round bar green compacts with an outer diameter of 12.5mm were prepared. On the other hand, the silver tube of the outer diameter of 16mm, the bore of 12mm, and die length 500 was produced with the unidirectional solidification process. Coagulation rates were 100 mm/min (sample 1), 20 mm/min (sample 2), 6.5 mm/min (sample 3), and 3 mm/min (sample 4). With the engine lathe, two tubing of the outer diameter of 15mm, the bore of 13mm, and die length 200 was produced about each sample from these silver tubes. Moreover, tubing of the same dimension was prepared using polycrystal **** as an object for comparison samples, and (the sample 6) was prepared for the thing with machining (sample 5), and the thing annealed 5h all over the 450-degree C vacuum furnace (0.001MPa). After inserting the above-mentioned round bar green compact in each above-mentioned silver tube and stopping both ends, it considered as the hexagon-head strand with an opposite side dimension of 2.55mm by CIP fabrication for the second time and wire drawing. Subsequently, these 19 strands were again enclosed with each silver tube, and it considered as the wire with an outer diameter of 1.5mm by the same processing method as hexagon-head strand formation. Strip processing of this wire was carried out, and it considered as the tape with 0.3mm [in thickness], and a width of face of 3mm. This tape was cooled to the room temperature after 100-hour heating in 840-degree C atmospheric air.

[0015] The superconduction property in 77K and 0T was measured with these wire rods' crystalline analysis of the superconductor according [using 100mm respectively] to X-ray analysis. The result is shown in Table 1. As shown in Table 1, they are the samples 2-4 (the amount of preferred orientation of the crystal face of a metal phase 95% or more) of an example. a and b-axis coherency 96% or more at 80% or more [the die length of a longitudinal direction] [the aspect ratio of 32mm or more, a longitudinal direction, and the cross direction] [whenever / or more 16 and c-axis oriented / of a superconducting phase] 105 A/cm2 High Jc of a more than It can realize, it also sets in a sample 1 (crystallinity is close to the threshold value of claim 1), and is 6x104 A/cm2. It becomes. On the other hand, the amount of preferred orientation of a metal phase is low, the amount of preferred orientation of a superconducting phase also falls rather than an example in connection with it by the samples 5 and 6 of the example of a comparison, and it is Jc. About 104 A/cm2 It is extent.

[0016]

表1

		結晶性					超電導特性	
		金属相			超電導相			
	試料No	配向度 %	粒寸法 長手 mm	幅 mm	配向度 C軸 %	a、b軸 %	T_c (K)	J_c (A/cm²)
実施例	1	95	4.5	1.1	95	76	110	6×10^4
	2	95	32	2.0	96	80	110	1×10^5
	3	97	100	2.5	98	85	110	5×10^5
	4	99	100	3.0	98	87	110	8×10^5
比較例	5	なし	0.4	0.5	80	60	108	2.5×10^4
	6	48	5	0.4	90	65	109	4.5×10^4

[0017] (Example 2) 99.99% of virgin silver and a silver-1.5wt% platinum alloy were prepared beforehand. It considered as the bar of a 6.5 mm outer diameter with the unidirectional solidification process respectively. However, each cooling rate was 2.5 mm/min in 20 mm/min and the latter at the former. This bar was used as the tape with 0.3mm [in thickness], and a width of face of 5mm with strip processing after wire drawing to the 2.6 mm outer diameter. On the other hand, the vacuum tub equipped with the RF suspension coil, the high-speed tape transit device, the preheater style, and the cooler style was prepared, and the following junction tape was produced using this equipment. That is, what was first blended so that it might be set to :(Bi+Pb) Sr:calcium:Cu=2:2:1:2 or 2:2:2:3 by the mole ratio as oxide superconductivity raw material powder was prepared, and the preforming object with an outer diameter [of 25.4mm] and a height of 25.4mm was produced with CIP shaping. This preforming object was made into about 935-degree C melt in the RF suspension coil of the ambient atmosphere of 0.003MPa and 0.001MPa, this melt was sprayed on said silver under transit, and a silver-platinum alloy tape by 25 m/s by which the preheating was carried out to 450 degrees C and 650 degrees C, and the amorphous junction tape of about 100-micrometer thickness was produced. This junction tape was taken out from the vacuum tub, reheating processing was carried out the following condition, and the oxide superconductive material was crystallized. That is, after 10min heating, to 700 degrees C, it cooled by 10 degrees C / min, and the 2212 phase system junction tape was cooled among the furnace to the room temperature after that in 890-degree C atmospheric air. On the other hand, the 2223 phase system junction tape was cooled to the after [24 hour maintenance] room temperature in 840-degree C atmospheric air. About these junction tapes, the superconduction property in 77K and 0T was measured with crystalline analysis. The conditions of the produced sample are shown in Table 2, and the crystallinity of these samples and a superconduction property are shown in Table 3.

[0018] As shown in Table 3, for the aspect ratio of 55mm or more, a longitudinal direction, and the cross direction, whenever [or more 27 and c-axis oriented / of a superconducting phase] is [the amount of preferred orientation of the crystal face of a metal phase / the die length of 95% or more and a longitudinal direction / 95% or more, a, and b-axis coherency] 75% or more, and samples 1-8 are 105 A/cm2. High Jc of a more than It was shown.

[0019]

表2

試料No	金属相ﾃｰﾌﾟ	酸化物超電導相	真空度 MPa	ﾃｰﾌﾟ予熱温度 ℃
1	Ag	2212	0.003	450
2	Ag	2212	0.003	650
3	Ag	2212	0.001	450
4	Ag	2223	0.003	450
5	Ag	2223	0.001	450
6	Ag-Pt	2212	0.003	450
7	Ag-Pt	2212	0.003	650
8	Ag-Pt	2223	0.003	650

[0020]
表3

試料No	結晶性					超電導特性
	金属相			超電導相		
	配向度	粒寸法 長手	幅	配向度 C軸	a、b軸	J_c
	%	mm	mm	%	%	(A/cm²)
1	96	55	2.0	98	80	3.1×10^5
2	96	55	2.0	98	85	5.5×10^5
3	96	55	2.0	98	87	7.5×10^5
4	96	55	2.0	95	80	8.5×10^5
5	96	55	2.0	96	83	11.3×10^5
6	97	80	2.5	95	75	2.6×10^5
7	97	80	2.5	98	80	4.7×10^5
8	97	80	2.5	97	85	12.2×10^5

[0021] (Example 3) Beforehand, a platinum wire rod with an outer diameter of 1.5mm is prepared with the polycrystalline substance, and it is CO2. Laser was heat-treated by coagulation rate 50 mm/min with the unidirectional solidification process in the atmospheric air made into the heat source. This wire rod was rolled out and it considered as the tape with 0.15mm [in thickness], and a width of face of 2.5mm. Moreover, according to the approach of an example 2, the silver-1.5wt% platinum tape of the same dimension was also prepared. Furthermore, the mole ratio prepared the preforming object with a diameter [of 25.4mm], and a height of 25.4mm adjusted to Y:Ba:Cu=1:2:3 as oxides superconductors. platinum tape [by which set this Plastic solid to the same vacuum tub as an example 2, and was made into about 1020 degrees C in the ambient atmosphere of 0.01MPa, 0.003MPa, and 0.001MPa, and the preheating was carried out to 500 degrees C under transit by 30m/s in rate after suspension melting], and silver-1.5wt% -- it sprayed on the platinum tape, and it quenched and the junction tape was

produced. Then, 8h of these junction tapes was annealed in the 450-degree C oxygen air current. About these junction tapes, the superconduction property in 77K and 0T was measured with crystalline analysis. The conditions of the produced sample are shown in Table 4, and the crystallinity of these samples and a superconduction property are shown in Table 5. As shown in Table 5, for the aspect ratio of 40mm or more, a longitudinal direction, and the cross direction, whenever [or more 13 and c-axis oriented / of a superconducting phase] is [the amount of preferred orientation of the crystal face of a metal phase / the die length of 95% or more and a longitudinal direction / 95% or more, a, and b-axis coherency] 75% or more, and samples 1-6 are 2.5x105 A/cm2. High Jc of a more than It was shown.

[0022]

表4

試料No	金属相ﾃｰﾌﾟ	真空度 MPa
1	Pt	0.01
2	Pt	0.003
3	Pt	0.001
4	Ag-3wt%Pt	0.01
5	Ag-3wt%Pt	0.003
6	Ag-3wt%Pt	0.001

[0023]

表5

試料No	結晶性					超電導特性
	金属相			超電導相		
	配向度	粒寸法 長手	幅	配向度 C軸	a、b軸	J_c
	%	mm	mm	%	%	(A/cm²)
1	95	40	3.0	95	75	2.5×10^5
2	95	40	3.0	95	80	5.5×10^5
3	95	40	3.0	97	80	9.8×10^5
4	96	45	2.0	96	77	3.5×10^5
5	96	45	2.0	97	80	6.7×10^5
6	96	45	2.0	99	85	12.1×10^5

[0024]

[Effect of the Invention] According to invention according to claim 1, a superconduction line is high Jc. There is outstanding effectiveness of having. Moreover, according to invention according to claim 2, improvement in the crystal orientation of oxides superconductors can be expected, and it is high Jc. The superconduction line which it has can be manufactured with sufficient productivity.

[Translation done.]